

REVIEW PAPER

Biochar composites: Emerging trends, field successes and sustainability implications

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Funding information

National Natural Science Foundation of China, Grant/Award Number: 42077118; National Key Research and Development Program of China, Grant/Award Number: 2020YFC1808000; Cooperative Research Program for Agriculture Science and Technology Development, Grant/Award Number: PJ01475801; Rural Development Administration, Republic of Korea

Abstract

Engineered biochars are promising candidates in a wide range of environmental applications, including soil fertility improvement, contaminant immobilization, wastewater treatment and in situ carbon sequestration. This review provides a systematic classification of these novel biochar composites and identifies the promising future trends in composite research and application. It is proposed that metals, minerals, layered double hydroxides, carbonaceous nanomaterials and microorganisms enhance the performances of biochars via distinct mechanisms. In this review, four novel trends are identified and assessed critically. Firstly, facile synthesis methods, in particular ball milling and co-pyrolysis, have emerged as popular composite fabrication strategies that are suitable for large-scale applications. Secondly, biochar modification with green materials, such as natural clay minerals and microorganisms, align well with the on-going green and sustainable remediation (GSR) movement. Furthermore, new applications in soil health improvement and climate change mitigation support the realization of United Nation's Sustainable Development Goals (SDGs). Finally, the importance of field studies is getting more attention, since evidence of field success is critically needed before large-scale applications.

KEYWORDS

climate change, field trial, life on lands, SDGs, soil quality, sustainable remediation

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1 | INTRODUCTION

Biochar is the solid material derived from various biomass feedstocks under oxygen-limited thermal conversion processes (IBI, 2015). Biochar is known to possess well-developed porous structures (Kwiatkowski & Kalderis, 2020; Leng et al., 2021), abundant functional groups (Ahmad et al., 2014; Wang, Ok, et al., 2020), various inorganic nutrients (Dai et al., 2020; Smider & Singh, 2014) and high carbon stability (Li et al., 2014; Spokas, 2010). Therefore, biochar can be used for various purposes, including soil fertility improvement (Arif et al., 2020; El-Naggar et al., 2019), contaminant immobilization (Palansooriya et al., 2020; Shen et al., 2018; Wang et al., 2020), wastewater treatment (Shaheen et al., 2019; Thompson et al., 2016; Xiang et al., 2020), flue gas purification (Shan et al., 2019; Shi et al., 2020) and in situ carbon storage (Han Weng et al., 2017; Hardy et al., 2017).

Although pristine biochar has shown excellent performance in environmental applications, the activation or modification of biochar to enhance its physicochemical properties has emerged as a new trend (Wang, Ok, et al., 2020). The term 'engineered biochar' is therefore used to represent these materials that have been modified or activated via physical, chemical or biological approaches for specific purposes (Kazemi Shariat Panahi et al., 2020; Ok et al., 2015; Wang et al., 2017). Numerous attempts have been made to activate biochar with gas, steam, microwaves, acids, alkalis and oxidants without the introduction of external doping agents (Panwar & Pawar, 2020; Sajjadi et al., 2019). Another route is to introduce materials other than biochar itself, and having distinct and useful properties, to fabricate composites.

Biochar composite promises much as a soil amendment, offering multifaceted benefits in both agriculture and environmental remediation. On the one hand, feeding 9 billion people by 2050 without exceeding the planetary boundary seems to be a tough challenge (Gerten et al., 2020; Godfray et al., 2010). Application of certain types of biochar composites directly improves the physical structure and the chemical fertility of soil, leading to enhanced crop yield. On the other hand, remediating the soils in a 'green and sustainable' manner also requires future development of novel materials (Hou, 2020; Wang et al., 2021). Engineered biochar composites loaded with key immobilization/degradation components assure the long-term remediation of contaminated soil with low life cycle impact. Furthermore, novel applications of biochar composites in other fields, such as energy storage and cement additive, have also emerged, leading to a 'green transition' in various disciplines (Atinafu et al., 2020; Gupta et al., 2018).

Although several studies have reviewed the fabrication methods and environmental applications of biochar composites, a systematic classification and the recognition of

emerging trends in biochar composite research are still lacking. Therefore, the motivation of this review is to provide a classification of biochar composites, along with a discussion of the enhancement mechanisms. Novel trends in composite fabrication and new uses in environmental applications are clarified. In addition, lessons from the field are critically summarized, and the ways in which biochar composites assist in the realization of a sustainable future are discussed.

2 | CLASSIFICATION AND ENHANCEMENT MECHANISMS

Biochar composites can be divided into five categories, including metal-biochar composites, mineral-biochar composites, layered double hydroxide (LDH)-biochar composites, carbonaceous engineering nano-composites and microorganism-biochar composites (Figure 1). Compared with the virgin biochar, biochar composites have shown excellent performances in various environmental applications (Figure 1). The enhancement mechanisms of each type will be discussed in the following subsections.

2.1 | Metal-biochar composites

Introducing iron species onto biochar has proven to be an effective means to enhance the performances of biochar. Nano zero valent iron (nZVI)-biochar, iron oxide-biochar and iron sulphide-biochar composites are the major composite types. Several articles have comprehensively reviewed the fabrication methods, enhancement mechanisms and environmental applications of iron-biochar composites (Lyu et al., 2020; Wang, Zhao, et al., 2019; Yi et al., 2019). In brief, iron-biochar composites favour the adsorption and immobilization of heavy metals and organic contaminants via enhanced surface complexation, precipitation and electrostatic interactions (Alam et al., 2020; He et al., 2018; Zhang, O'Connor, et al., 2020). Certain types of iron-biochar composites, such as nZVI-biochar and FeS-biochar have a high reduction potential towards organic contaminants and the Cr(VI), since they can provide Fe(0), Fe(II) and S(II) species (Chen et al., 2020; Liu et al., 2020; Lyu et al., 2018). Iron-biochar composites can also activate oxidants to generate reactive oxygen species (ROS) for the oxidation of organic contaminants (Diao et al., 2020; Park et al., 2018). It is noteworthy that multiple iron species may be present in iron-biochar composites simultaneously, enhancing the performances of biochar through various mechanisms. For instance, Fe(II) species on the surface of FeCl₃-soaked biochar were found to be responsible for Cr(VI) reduction, whereas Fe(III) species would

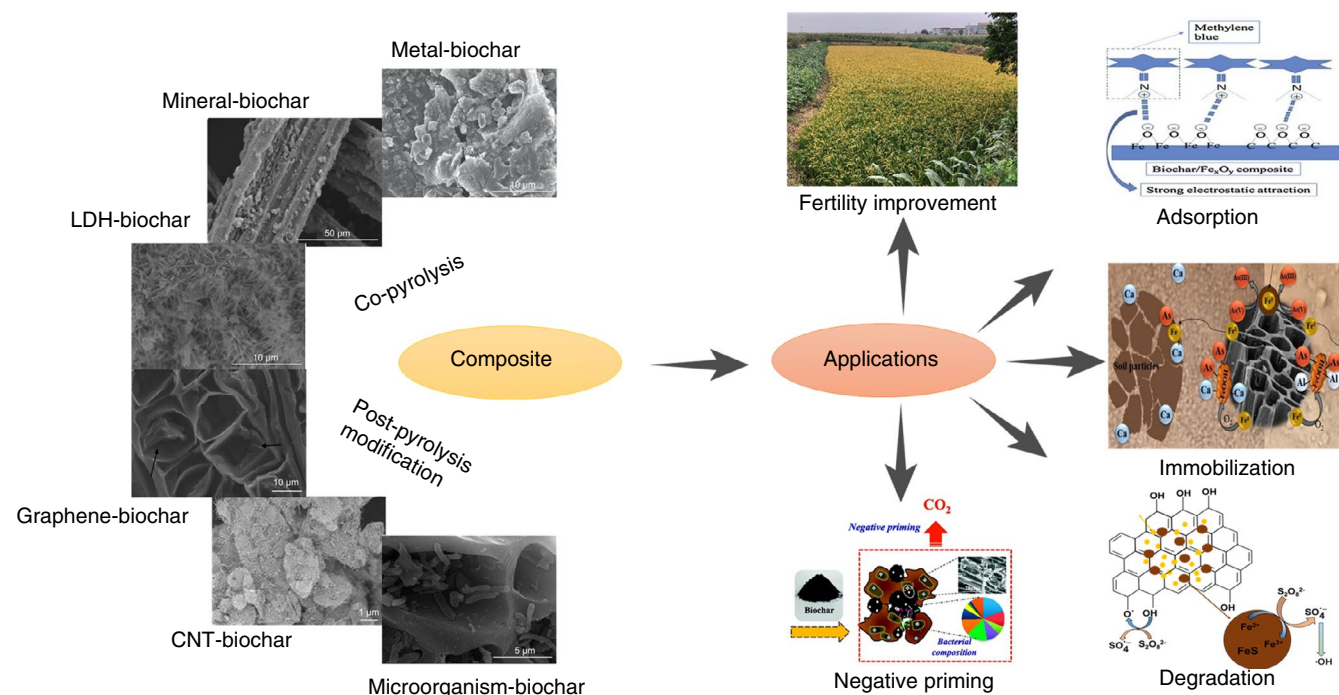


FIGURE 1 various types of engineered biochar composites with distinct surface morphologies and their environmental applications. metal-biochar: mgo-coated corncob biochar composite for pb stabilization in clayey soil. hexagonal and cubic mgo particles were well dispersed on the biochar (shen 2019). mineral-biochar: montmorillonite-biochar composite for slow release of ammonium and phosphate. montmorillonite particles were observed on the surface of bamboo biochar, but did not completely cover the surface (chen et al., 2017). ldh-biochar: ni-fe ldh-biochar composite for phosphate adsorption. ldh flakes were attached to corn stalk biochar (yang et al., 2019). graphene-biochar: graphene-coated cotton wood biochar for methylene blue adsorption (zhang e., 2012). cnt-biochar: multiwalled carbon nanotube (mwcnt)-biochar composite for the encapsulation of phase change material to store thermal energy. a tubular surface morphology was observed (atinafu et al., 2020). microorganism-biochar: bacterium delftia sp. b9-inoculated corn stalk biochar for cd immobilization in soil. the cells were attached to the pores (liu, tie, et al., 2020). all images were reproduced with permission

precipitate with the as-formed Cr(III) (Chen et al., 2020). Iron in different forms, including mining and industrial residues, can be successfully used as a dopant to improve biochar performance in the removal of contaminants, offering a potentially attractive circular economy option (Wurzer & Mašek, 2021).

Apart from iron-biochar composites, other types of metal-biochar composites, such as MgO-biochar composites, MnO_x-biochar composites and MoS₂-biochar composites, are also innovative candidates in environmental applications. Shen et al. (2019) fabricated MgO-coated biochar for Pb immobilization in clayey soil. The biochar matrix adsorbed Pb onto its surface via cation- π interactions, while MgO enhanced Pb immobilization through precipitation. Yu et al. (2017) loaded manganese oxide onto biochar through soaking with KMnO₄. The resulting biochar composite successfully immobilized soil As because of the oxidation of As(III) to As(V). Yang et al. (2020) synthesized a novel g-MoS₂ coated biochar nano-composite for ciprofloxacin adsorption. Compared with the virgin biochar, the composite provided more π electrons, enhancing the π - π EDA interactions.

It is noteworthy that co-doping biochar with various metals has emerged as a novel trend (Rajapaksha et al., 2016). Mg-Al biochar composites exhibited high phosphate adsorption capacity because of chemical precipitation (i.e., the formation of AlPO₄ and Mg₃(PO₄)₂) (Zheng et al., 2020). A Mg-Fe biochar composite reduced soil Cd bioavailability through enhanced surface complexation and ion exchange (Gao et al., 2019). A Fe-Mn biochar composite immobilized soil As through triggering the formation of stable hydrous oxide-bound As forms (Lin et al., 2019), while Fe-Mn-Ce biochar composite was also proven to immobilize soil As because of the same mechanism (Zhang et al., 2020). A CuZnFe₂O₄-biochar composite promoted the adsorption of bisphenol A and sulfamethoxazole through hydrogen bonding, hydrophobic interactions and π - π EDA interactions (Heo et al., 2019). Metal co-doping is a facile method for the enhancement of biochar properties. This method has proven effective in environmental remediation. More studies should be conducted to examine the feasibility in other applications. For instance, it is suggested that co-doping nutrients, such as K, Ca and Mg, onto biochar may directly promote soil fertility and

TABLE 1 Various mineral-biochar composites and enhancement mechanisms

Mineral	Biochar feedstock	Preparation method	Enhancement mechanism of mineral	Environmental application	Performance	References
Attapulgite (palygorskite)	ZnCl ₂ -activated rice straw	Co-pyrolysis	To promote surface complexation	To immobilize As and Cd in a river sediment	Decreasing concentrations of As and Cd in sediment pore water by 82% and 48%, respectively compared with sediment treated with unmodified biochar	Wang, Gu, et al. (2019)
Attapulgite (palygorskite)	Cauliflower leaves	Co-pyrolysis	To provide oxygen-containing functional groups for organic contaminant adsorption	To adsorb oxytetracycline in the aqueous media	Adsorption capacity 33.3 mg g ⁻¹	Wang, Yang, et al. (2019)
Kaolinite	Sawdust	Mixing kaolinite with sawdust, and produce ceramics	To enhance contaminant adsorption ^a	To act as ceramic filters producing safe drinking water	Removing total hardness, total dissolved solids and turbidity by 42%, 46% and 67%, respectively	Chaukura et al. (2020)
Kaolinite	Pine cone seeds	Co-pyrolysis	To enhance contaminant adsorption ^b	To adsorb ivermectin in the aqueous media	Adsorption capacity 115.8 µg g ⁻¹	Olu-Owolabi et al. (2020)
Montmorillonite	Bark chip	Mixing clay suspension with biochar	To promote cation exchange	To immobilize Cu, Zn and Pb in an acidic soil	Reducing metal leaching by 100%, 100% and 52% for Cu, Zn and Pb, respectively (SPLP leaching test)	Arabyarmohammadi et al. (2018)
Montmorillonite	Bamboo	Co-pyrolysis	To promote cation exchange	To act as a slow-release fertilizer	Releasing NH ₄ ⁺ slowly (0.3–4.9%) with 2–88 h	Chen et al. (2017)
Montmorillonite	Rice husk	Mixing clay suspension with biochar	To provide silicon	To immobilize soil As via adsorption onto Si-ferrihydrite complex	Decreasing As(III) in the rice rhizosphere by 73%, compared with the untreated soil	Herath et al. (2020)
Montmorillonite	Corn straw	Co-pyrolysis	To promote cation exchange and surface complexation (with hydroxyl)	To adsorb Zn(II) in the aqueous media	Adsorption capacity 8.2 mg g ⁻¹	Song et al. (2020)
Struvite	Wheat straw	Co-precipitation formation of struvite onto biochar	To provide PO ₄ ³⁻ for fertility improvement	To act as a slow-release fertilizer	Releasing phosphorus continuously for over 56 days	Hu et al. (2019)
Struvite	Bamboo	Co-precipitation formation of struvite onto biochar	To provide PO ₄ ³⁻ for Cu precipitation	To immobilize soil Cu	Reducing acid-soluble Cu fractions by 47%, compared with the untreated soil	Li, Wang, et al. (2020)

^aFor this ceramic material, biochar rather than mineral acted as an enhancement additive.^bFor this composite material, biochar served as an enhancement additive improving the adsorption capacity of kaolinite.

TABLE 2 Environmental applications of LDH–biochar composites

LDH type	Biochar	Environmental application	The role of LDH	Performance	References
Ca-Al	Invasive plant <i>Solidago Canadensis</i>	Adsorption of Eu(III) in the aqueous media	To provide hydroxyl for surface complexation and anions for co-precipitation	Adsorption capacity 99 mg g ⁻¹	Li, Dong, et al. (2020)
Cu-Al	Rice husk	Adsorption of Malachite Green in the aqueous media	Not mentioned	The adsorption capacity increased from 59.5 mg g ⁻¹ to 471.0 mg g ⁻¹ after LDH attachment onto biochar	Palapa et al. (2020)
Mg-Al	Bovine bone	Adsorption of phosphate in the aqueous media	Not mentioned	Adsorption capacity 26.2 mg g ⁻¹	dos Santos Lins et al. (2019)
Mg-Al	Bovine bone	Adsorption of Methylene Blue in the aqueous media	Not mentioned	Adsorption capacity 406.5 mg g ⁻¹	Meili et al. (2019)
Mg-Al	Bamboo	Adsorption of phosphate in the aqueous media	To increase anion exchange capacity and enhance phosphate precipitation (with Mg ²⁺ and Al ³⁺)	Adsorption capacity 172 mg g ⁻¹	Wan et al. (2017)
Mg-Al	Cotton wood	Adsorption of phosphate in the aqueous media	Not mentioned	Adsorption capacity 410 mg g ⁻¹	Zhang et al. (2013)
Mg-Al	Date palm	Adsorption of Methylene Blue in the aqueous media	To improve the pore structure, thus enhance pore-filling; to enhance π - π interactions	The adsorption capacity increased from 206.6 mg g ⁻¹ to 302.8 mg g ⁻¹ after LDH attachment onto biochar	Zubair et al. (2020)
Mg-Fe	Pine biochar, pyrolysis temperature 300°C	Adsorption of phosphate in the aqueous media	To provide hydroxyl for surface complexation	The adsorption capacity increased from 1.4 mg g ⁻¹ to 17.5 mg g ⁻¹ after LDH attachment onto biochar	Bolbol et al. (2019)
Mg-Fe	Oil-tea camellia shells	Adsorption of Pb(II) in the aqueous media	To provide anions for co-precipitation	The adsorption capacity increased from 67 mg g ⁻¹ to 476 mg g ⁻¹ after LDH attachment onto biochar	Jia et al. (2019)
Mg-Fe	Wheat straw	Adsorption of nitrate in the aqueous media	To increase anion exchange capacity	Adsorption capacity 24.8 mg g ⁻¹	Xue et al. (2016)
Mg-Fe	Rice straw	Metal immobilization and nutrient retention in soil	To enhance surface complexation, anion exchange, hydrogen bonding, micropore filling, isomorphous substitution, and precipitation	Leaching of NH ₄ ⁺ , NO ₃ ⁻ , and metals decreased by 60%, 40%, and >90%, respectively after composite addition	Zhang et al. (2018)

(Continues)

TABLE 2 (Continued)

LDH type	Biochar	Environmental application	The role of LDH	Performance	References
Mn-Al	Oil-tea camellia shells	Adsorption of Cu(II) in the aqueous media	To provide anions for co-precipitation; isomorphic substitution of Mn(II) with Cu(II)	The adsorption capacity increased from 10.1 mg g ⁻¹ to 74.1 mg g ⁻¹ after LDH attachment onto biochar	Wang et al. (2018)
Ni-Fe	Pine wood	Adsorption of As in the aqueous media	To increase anion exchange capacity and provide hydroxyl for surface complexation	The adsorption capacity increased from 0.2 mg g ⁻¹ to 4.4 mg g ⁻¹ after LDH attachment onto biochar	Wang et al. (2016)
Zn-Al	Corn stalk	As immobilization in red and calcareous soils	To increase anion exchange capacity and provide hydroxyl for surface complexation	Compared with the virgin biochar, As concentrations in the water leachates in red soils and calcareous soils decreased by 53% and 54%, respectively for LDH-biochar composite	Gao et al. (2020)
Zn-Al	Corn stalk	Adsorption of phosphate in the aqueous media	To increase anion exchange capacity and provide hydroxyl for surface complexation	Excellent adsorption capacity of 152.1 mg g ⁻¹ and fast adsorption kinetics of 5925 mg g ⁻¹ h ⁻¹	Yang et al. (2019)

simultaneously enhance biochar carbon sequestration potential (Mašek et al., 2019). If properly designed, co-doped biochars could immobilize metals in soil while simultaneously releasing nutrients (Igalavithana et al., 2017).

2.2 | Mineral-biochar composites

Natural minerals can promote the performance of biochar during soil remediation, resulting in fertility improvements, and assist in wastewater treatment (Table 1). Montmorillonite, a typical clay mineral having a 2:1 sheet structure, could adsorb metals and retain cationic nutrients effectively via cation exchange with hydrated Na⁺, K⁺, Mg²⁺ and Ca²⁺ in the interlayer spaces (Brigatti et al., 2006; Rumble et al., 2018; Wang et al., 2020). For instance, bark chip biochar with montmorillonite immobilized soil Cu, Zn and Pb effectively because of cation exchange (Arabyarmohammadi et al., 2018). Co-pyrolysed bamboo biochar-montmorillonite acted as a slow-release fertilizer for NH₄⁺ (Chen et al., 2017). Instead of making use of the cation exchange mechanism, Herath et al. (2020) considered montmorillonite to be a silicon source. Soil As could be effectively immobilized via the formation of Si-ferrihydrite complex on the Si-rich montmorillonite-biochar composite. Attapulgite (palygorskite), a fibrous clay mineral with lamellar structure, has also attracted much attention because of its abundant hydroxyl groups. Attapulgite-biochar composites have proven effective for the immobilization of As and Cd in river sediments because of enhanced surface complexation (Wang, Gu, et al., 2019), and for the adsorption of oxytetracycline in the aqueous media because of enhanced π - π EDA interactions and the formation of hydrogen bonds (Wang, Yang, et al., 2019). Struvite (NH₄MgPO₄) is a nutrient-rich mineral that has been commonly used as a fertilizer. Co-precipitation of struvite directly onto biochar could enhance the slow release of PO₄³⁻, favouring fertility improvement (Hu et al., 2019) and metal immobilization (Li, Wang, et al., 2020). Mineral additives can also reduce potential toxicity of biochar produced from waste materials, thus enabling an otherwise unutilized resource to be brought to beneficial use (Mumme et al., 2018).

2.3 | LDH-biochar composites

Layered double hydroxides (LDHs) are anionic clay minerals consisting of positively charged metal hydroxide layers and anions in the interlayer space for charge neutralization (Ma et al., 2016; Wang & Ohare, 2012). A wide variety of LDH-biochar composites having different divalent and trivalent metal cations (e.g., Mg-Al, Mg-Fe, Zn-Al, Ca-Al, Ni-Fe) have been widely used in contaminant adsorption

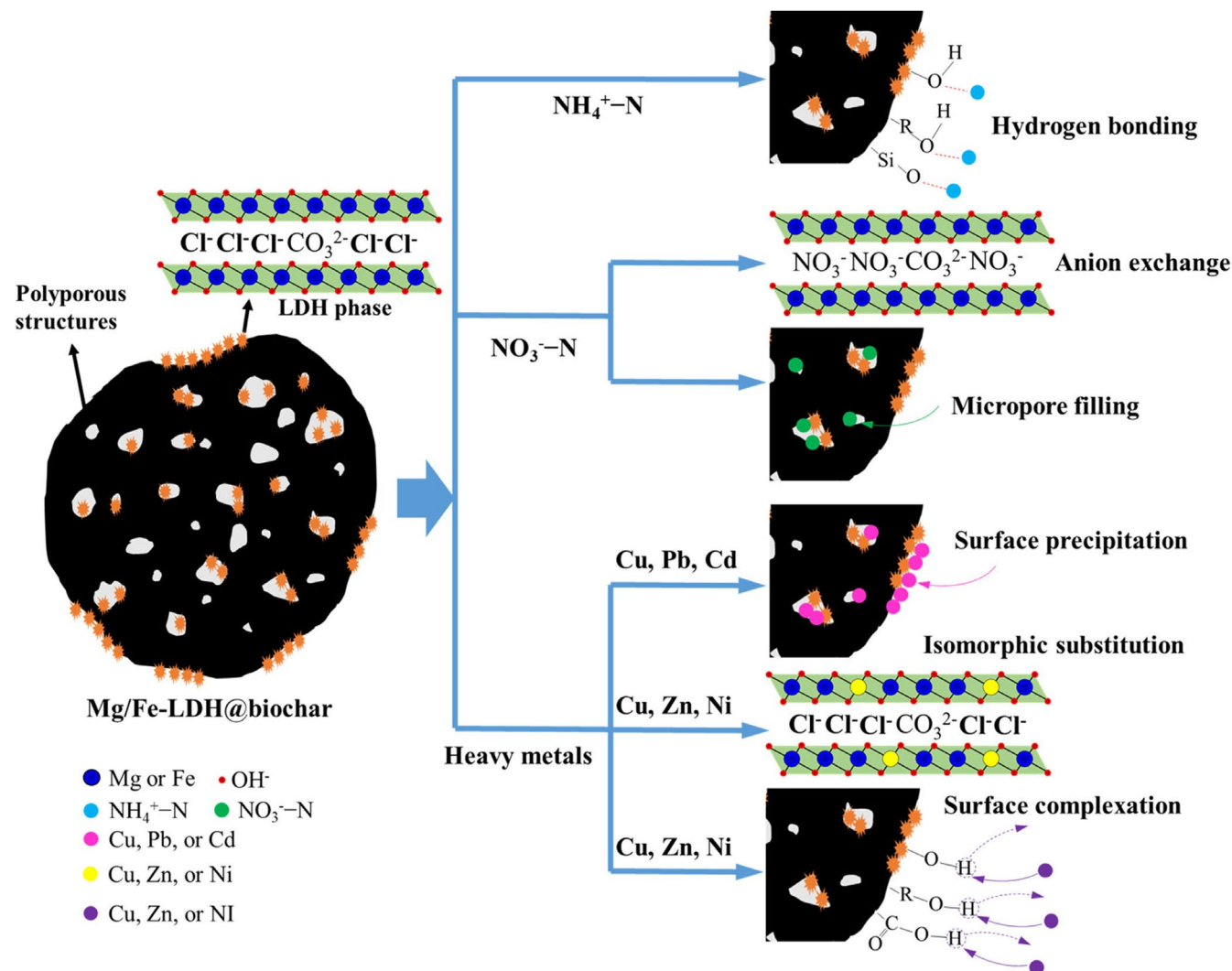


FIGURE 2 Possible metal and nutrient retention mechanisms of Mg/Fe-LDH biochar composites. Metals can be immobilized via strong interactions including surface complexation, precipitation and isomorphous substitution in the long run, while nutrients adsorbed via hydrogen bonding, anion exchange and micropore filling can be released slowly. Reproduced with permission from Zhang et al. (2018). Copyright 2018 American Chemical Society

(Table 2). The enhancement mechanisms include providing hydroxyl groups for surface complexation (Bolbol et al., 2019) and hydrogen bonding (Zhang et al., 2018), increasing anion exchange capacity (Gao et al., 2020) and enhancing co-precipitation (Wan et al., 2017). Because of the high anion exchange capacity of LDH-biochar composites, these materials have been extensively used for the adsorption of anionic contaminants, including phosphate (Yang et al., 2019), nitrate (Xue et al., 2016) and arsenic (Wang et al., 2016) (Table 2). Notably, LDH-biochar composites can also be used for the adsorption of organic contaminants because of pore-filling, π - π EDA interactions and hydrogen bonding (Meili et al., 2019; Zubair et al., 2020). LDH-biochar composites can simultaneously immobilize metals while improving nutrient retention because of the multifaceted enhancement mechanisms (Figure 2, section 4). Zhang et al. (2018) observed that heavy metals in soil, including

Cu, Zn, Ni, Cd and Pb, would be immobilized via strong interactions such as surface complexation, precipitation and isomorphous substitution, while nutrients, such as NH_4^+ and NO_3^- would be adsorbed through much weaker interactions (i.e., hydrogen bonding, anion exchange and micropore filling) (Figure 2). Therefore, soil metals could be immobilized in the long run, while nutrients would be released slowly.

2.4 | Carbonaceous engineered nano-composites

Graphene-biochar and carbon nanotube (CNT)-biochar composites enhance the adsorption of organic contaminants. The abundance of π electrons in these carbonaceous engineered nano-composites contribute to their excellent adsorption performance. The high adsorption capacity of

TABLE 3 The aims of microorganism colonization for biochar modification

Aim	Microorganism	Biochar	Performance	Enhancement mechanism	References
To enhance the biodegradation of dibutyl phthalate (DBP) in soil	<i>Bacillus siamensis</i>	Rice husk biochar, pyrolysis temperature 500°C, heating rate 8°C·min ⁻¹ , residence time 3 h	Raising the degradation rate constant of DBP from 0.11 day ⁻¹ to 0.24 day ⁻¹ compared with the virgin biochar	To degrade DBP directly	Feng et al. (2020)
To immobilize soil Cd	<i>Delftia</i> sp. B9	Corn stalk biochar, pyrolysis temperature 500°C, residence time 2 h	Decreasing the Cd concentration in rice grains by 79% compared with the unamended soil	Not investigated	Liu, Tie, et al. (2020)
To immobilize soil Cd	<i>Bacillus</i> sp. TZ5	Coconut shell biochar, pyrolysis temperature 800°C, residence time 6 h	Increasing the biomass of ryegrass by 78%, while decreasing the Cd concentration by 48% compared with the unamended soil	To provide carbonyl, hydroxyl and amide functional groups for surface complexation	Ma et al. (2020)
To immobilize soil Cu and Cd	<i>Pseudomonas</i> sp. NT-2	Maize straw biochar, pyrolysis temperature 400°C, residence time 8 h	Decreasing DTPA-extractable Cu and Cd by 15% and 19%, respectively, compared with the virgin biochar	To provide hydroxyl, carboxyl, and amine functional groups for surface complexation; to release phosphate for metal precipitation	Tu et al. (2020)
To adsorb As and Cd in the aqueous media	<i>Bacillus</i> sp. K1	Rice straw biochar, pyrolysis temperature 500°C, heating rate 10°C·min ⁻¹ , residence time 2 h	Adsorption capacity 25.04 and 4.58 mg g ⁻¹ for Cd and As, respectively	To provide hydroxyl and amine functional groups for surface complexation	Wang, Li, et al. (2021)
To improve grape quality	<i>Pseudomonas putida</i> Rs-198	Bamboo biochar	Increasing the grape weight by 7.6% compared with the unamended soil	To release phosphate and fix nitrogen for fertility improvement	Wei et al. (2020)
To degrade polycyclic aromatic hydrocarbons (PAHs) in soil	<i>Mycobacterium gilvum</i>	Rice straw biochar, pyrolysis temperature 500°C, residence time 4 h	Decreasing the concentrations of phenanthrene, fluoranthene and pyrene by 58%, 49% and 56%, respectively, compared with the virgin biochar	To degrade PAHs directly	Xiong et al. (2017)

graphene nanosheet–biochar composites for phthalic acid esters has been attributed to enhanced hydrophobic interactions, and π - π EDA interactions (Abdul et al., 2017; Zhang et al., 2012). Graphene oxide (GO)-biochar composites promotes the adsorption of sulfamethazine mainly via π - π EDA interactions, while pore-filling, ion exchange and hydrogen bonding also play a vital role (Huang et al., 2017). Multiwalled carbon nanotube (MWCNT)–biochar composites revealed excellent adsorption performance towards methylene blue because of electrostatic interactions (Inyang et al., 2014). Interestingly, an engineered MWCNT–biochar composite had an excellent encapsulation capacity of n-dodecane, a phase change material for energy storage. It could be that the biochar composite possessed stable networks, favouring the attachment of organic molecules by surface tension and capillary forces (Atinafu et al., 2020).

Carbonaceous engineered nano-composites have been used for the remediation of metals. Inyang et al. (2015) fabricated a novel MWCNT–biochar composite for the simultaneous removal of Pb and sulphapyridine in the aqueous media. The enhancement mechanisms of organic contaminant adsorption were attributed to the aforementioned π - π EDA interactions and hydrogen bonding, while Pb removal was possible because of surface complexation with oxygen-containing functional groups. Apart from surface complexation, Liu et al. (2016) suggested that the mechanisms enhancing adsorption by GO- and CNT-biochar composites also include cation- π interactions.

2.5 | Microorganism–biochar composites

Microorganisms can improve the performances of biochar in removing contaminants in three ways (Table 3). Firstly, inoculation of microorganisms having high degradation capabilities for organic contaminants onto a biochar enhances the overall biodegradation directly. For instance, rice husk biochar inoculated with the dibutyl phthalate (DBP)-degrading strain *Bacillus siamensis* showed elevated contaminant degradation, with the rate constant increasing from 0.11 day⁻¹ for the biochar alone to 0.24 day⁻¹ (Feng et al., 2020). Another study by Xiong et al. (2017) found that engineered *Mycobacterium gilvum*-rice straw biochar composite degraded soil polycyclic aromatic hydrocarbons (PAHs) more effectively than the unmodified biochar.

Second, considering that microbial cells are rich in various oxygen- and nitrogen-containing functional groups, including carbonyl, hydroxyl and amine, several studies have used microorganism-biochar composites for soil metal immobilization. Heavy metals and metalloids, such as Cu, As and Cd, can be immobilized via surface complexation (Ma et al., 2020; Tu et al., 2020; Wang, Li, et al., 2021). Third, the phosphate released from the microorganisms can also immobilize soil metals via precipitation (Tu et al., 2020).

Microorganism–biochar composites can also be used for soil fertility improvement because of the ability of microorganisms to release phosphate and fix nitrogen (Wei et al., 2020).

2.6 | Other types

Considering that wood biochars possess relatively low nutrient contents for soil fertility improvement, Buss et al. (2019) applied an ash–biochar composite to infertile soil. Rather than the rapid release of nutrients by direct application of plant ash, the biochar composite released nutrients much more slowly. This was because the original wood ash (obtained from a heating plant with steam temperature 140°C) with similar characteristics with biomass feedstock could be further transformed to a more stable form, namely charcoal after co-pyrolysis. Liu et al. (2019) synthesized a novel composite consisting of biochar, urea, bentonite and polyvinyl alcohols for the controlled release of nitrogen. Wang et al. (2018) modified biochar with calcium alginate to improve the water and nutrient retention capabilities via swelling and ion exchange, respectively. Zhao, Cao, et al. (2016) co-pyrolysed sawdust and switchgrass biomass directly with phosphate fertilizers to produce engineered composites for nutrient release and metal immobilization. Without doubt, novel biochar composites would emerge, together with novel synthesis methods (section 3) and applications (section 4).

3 | EMERGING TRENDS IN COMPOSITE SYNTHESIS

Biochar composites can be synthesized either via co-pyrolysis or post-pyrolysis modification (Mandal et al., 2020; Tan et al., 2016). In the former approach, enhancement agents, such as metal oxides and minerals, are doped to the biochar feedstock prior to pyrolysis. In contrast, more studies tend to adopt the latter method of post-pyrolysis biochar modification. Considering that the biochar-producing process involves high temperatures, the feasibility of the introduction of certain chemicals is limited. For instance, biochar–goethite composites having excellent As adsorption and immobilization performances could only be synthesized using post-pyrolysis modification, since goethite (α -FeOOH) would be transformed into hematite (α -Fe₂O₃) if the temperature reaches 260–280°C because of dehydration (Ammasi, 2020; de Faria & Lopes, 2007). For a comprehensive view on conventional biochar composite synthesis methods, readers are referred to Mandal et al. (2020).

Green fabrication has emerged as a novel trend in biochar composite synthesis, aligning well with the green chemistry concept. In the context of biochar composite synthesis, a green fabrication method should use safer

chemicals and milder reaction conditions (USEPA, 2017). For instance, Zhang, O'Connor, et al. (2020) used banana peel extracts rather than toxic NaBH_4 for nZVI loading onto the resulting banana peel biochar. After that, the dissolved oxygen in water could oxidize nZVI into iron oxides. The as-formed biochar-iron oxide composite could adsorb methylene blue more effectively than the pristine biochar. Instead of pyrolysing the feedstock under high temperatures (i.e., $>300^\circ\text{C}$), another study by Zhang et al. (2020) prepared the S-Fe-biochar composite using a one-step hydrothermal method, lowering the reaction temperature to 180°C , while simultaneously introducing Fe and S to the biochar.

It is noteworthy that ball milling, a green and facile physical modification method, has proven successful for biochar composite fabrication. Compared with conventional chemical modification approaches, ball milling is a solid-to-solid modification method that avoids the introduction of toxic chemicals. Typically, the internal barrel of the ball mill can be separated into four zones, namely the cascading zone, the cataracting zone, the fracture zone and the grinding zone (Figure 3) (Peng et al., 2017). The combined effects of four zones lead to the thorough mixing of biochar and the chemicals, while the fracture zone and grinding zone play significant roles in the downsizing process. Because of grinding and fracturing, the sizes of particles can be reduced simultaneously during ball milling, thus increasing the reactivity and producing nano-sized biochar composites. He et al. (2021) synthesized a FeS-biochar composite after milling FeS and biochar with zirconia balls for 12 h. Scanning electron microscopy analysis indicated the fracture and deformation of the original large block structures of both materials into nano-sized particles, while X-ray diffraction analysis confirmed the doping of FeS onto biochar. Li, Wan, et al. (2020) found that ball milling could extrude biochar into the interlayers of vermiculite (a typical 2:1 clay mineral), forming a novel biochar-clay nano-composite efficient in

As(V) adsorption. Wang et al. (2020) also noticed that ball milling resulted in the formation of the nanoparticles of Fe(0)-biochar composites with excellent Cr(VI) reduction performances. It is concluded that biochar composite synthesis methods tend to be more environmentally friendly and facile. Physical modification methods, rather than chemical doping approaches, appear to be more viable.

4 | NEW APPLICATIONS IN SOIL HEALTH IMPROVEMENT AND CLIMATE CHANGE MITIGATION

In recent years, soil health has emerged as the most widely acknowledged concept in terms of sustainable utilization of valuable soil resources and tackling the soil constraints, and has caused a global evolution of traditional soil use and management strategies towards a more sustainable manner (Hou et al., 2020). Soil health has been defined as '*the capability of soil to function as a living system*' (FAO, 2011). However, soils from all parts of the world, in particular East Asia, South Asia, East Australia, Central Africa and South America (Figure 4), suffer from various constraints, including physical ones such as poor soil structure and water holding capacity, chemical ones such as nutrient loss and contamination, and biological ones such as soil pathogens and faunal reduction (FAO, 2015). New applications of biochar composites to improve soil health include physical structure enhancement (section 4.1), metal immobilization in soil (section 4.2), organic contaminant degradation/retention (section 4.2), water and nutrient retention (section 4.3), salinity adaptation (section 4.4) and antibiotic resistance gene suppression (section 4.5), ultimately assisting the soil to 'act as a living system'. Global climate change is an immense challenge, attracting researchers from all disciplines. In the context of soil use and management, the application of novel biochar composites also helps to mitigate climate change.

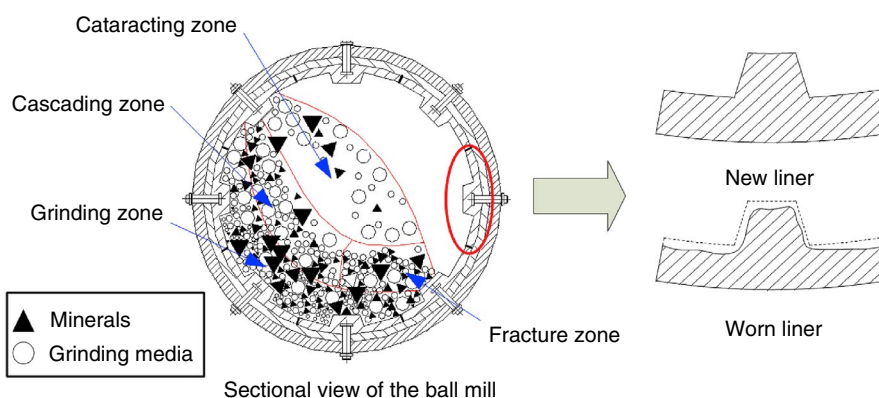


FIGURE 3 A mechanistic understanding of the ball milling process, an emerging physical method to fabricate biochar composites. The combined effects of four zones, including the cataracting, cascading, grinding and the fracture zone, contribute to thorough mixing. Reproduced with permission from Peng et al. (2017). Copyright 2017 Elsevier

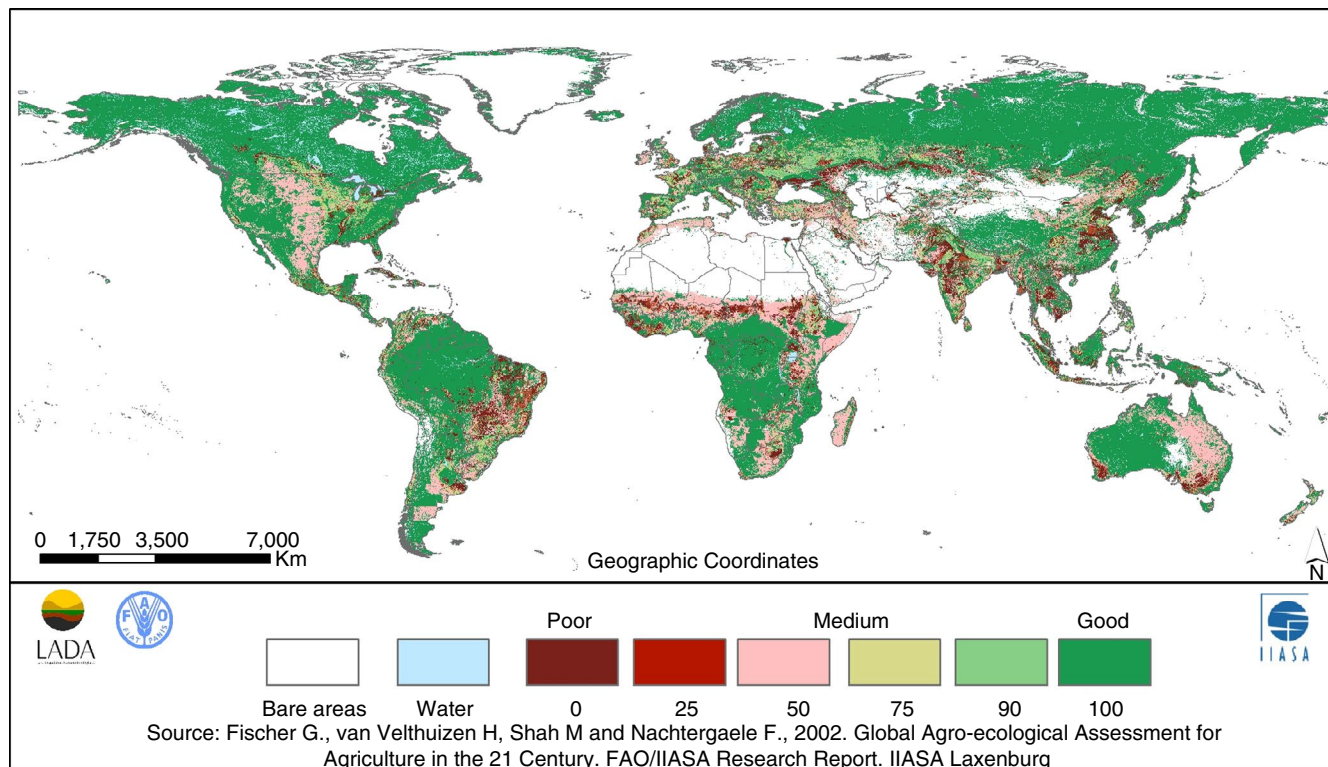


FIGURE 4 Soil health status for present land use. Copyright FAO

The following subsection discusses novel applications of biochar composites for climate change mitigation (section 4.6).

4.1 | Soil physical structure enhancement

Application of unmodified biochar has been acknowledged as an effective means to enhance the physical structure of soils (Herath et al., 2013; Hou, Wang, et al., 2020). The comprehensive review by Blanco-Canqui (2017) suggested that fresh biochar application increases soil porosity by 14% to 64%, while reducing soil bulk density by 3% to 31%. Furthermore, biochar application can enhance soil aggregation, which could be that organic carbon particles can form ligands with soil particles (Blanco-Canqui, 2017). Although biochar itself has already shown excellent performances in soil aggregation, a recent study by Liu, Kong, et al. (2020) indicated that application of Fe-biochar composite increased the stability of soil aggregates. This was attributed to the fact that iron oxides on the biochar surface induced co-precipitation with soluble organic carbon in the soil solution, while simultaneously acting as a cementing agent for soil aggregate formation (Liu, Kong, et al., 2020). In addition, considering that organo-mineral interaction is the key factor controlling soil aggregation (Possinger et al., 2020), it is proposed that mineral-biochar composites can also improve the physical properties of the amended soil. More evidences from the lab and the field are required to further test this hypothesis.

4.2 | Contaminant remediation

Although biochar alone has revealed its potential in soil metal immobilization, biochar modification to produce engineered composites is a feasible way to improve the performance of biochar. Biochar composites aid in metal immobilization in various ways. For instance, iron-biochar composites promote the stabilization of both cations (e.g., Cd, Pb) and oxyanions (e.g., As, Sb) via enhanced surface complexation (Gao et al., 2019; Qiao et al., 2018; Teng et al., 2020). Ash-biochar composites with high alkalinity increase soil pH, favouring the electrostatic interactions for metallic cations and negatively charged soil colloids (Lei et al., 2020). Nano zero valent iron- and iron sulphide-biochar composites promote soil Cr(VI) reduction (Liu, Yang, et al., 2020; Lyu, Zhao, et al., 2018; Wang et al., 2019). In particular, immobilization of soil As with unmodified biochar seems impractical (Beiyuan et al., 2017). An elevated soil pH resulting from biochar addition would mobilize the arsenate oxyanions (e.g., H_2AsO_4 and H_2AsO_4^-) in turn (Bandara et al., 2020; Vithanage et al., 2017). Many attempts have been made to discover novel biochar composites to immobilize soil As. The LDH-biochar composites immobilize As because of their high anion exchange capacity and high abundance of surface hydroxyl functional groups that promote both inner- and outer-sphere surface complexation (Gao et al., 2020). Iron-biochar composites are the most promising candidate in soil As immobilization. It has been

recognized that As will form stable inner-sphere complexes with iron oxides (such as FeOOH and Fe₂O₃) via ligand exchange with surface hydroxyl groups of the FeO₆ octahedra (Dixit & Hering, 2003; Sherman & Randall, 2003). Indeed, iron-oxide biochar composites have successfully stabilized As (Lin et al., 2017). Precursors of iron oxides, including ZVI and iron sulphates, can be used to form iron-biochar composites for As immobilization (Fan et al., 2020). Further insights on metal immobilization performances of engineered biochar composites, readers are referred to Wang, Ok, et al. (2020) and Rajapaksha et al. (2016).

Apart from metal immobilization, novel biochar composites have been successfully used for organic contaminant remediation. Microorganism-inoculated biochar has shown excellent contaminant degradation performance. For instance, rice husk biochar inoculated with the dibutyl phthalate (DBP)-degrading strain *Bacillus siamensis* boosted DBP degradation while simultaneously restricting plant uptake of this contaminant (Feng et al., 2020). During this process, biochar acted in a secondary role; that is, it provided the supporting matrix to adsorb and retain DPB (Feng et al., 2020). Another study by Xiong et al. (2017) applied *Mycobacterium gilvum*-inoculated biochar to a soil contaminated by PAHs. Biochar facilitated the mass transfer of PAHs from soil to the carbonaceous matrix, where these contaminants could be degraded by the inoculated microorganisms.

Metal-biochar composites immobilize organic contaminants via various mechanisms, including adsorption, plaque formation and microbial stimulation. Biochar-supported CuZnFe₂O₄ composites were shown to adsorb bisphenol A and sulfamethoxazole via enhanced hydrogen-bonding and π - π EDA interactions (Heo et al., 2019). A MoS₂ nanosheet-biochar composite could adsorb ciprofloxacin more effectively than the corresponding pristine biochar by a factor of 5.5. In this case, the abundance π electrons of the nanosheet promoted π - π EDA interactions (Yang et al., 2020). Iron oxide-biochar composite application resulted in the formation of an iron plaque within the rhizosphere, reducing the uptake of the pesticide chlorpyrifos by *Allium fistulosum* (Welsh onion) (Tang et al., 2017). Iron oxide-biochar composites can also stimulate the biodegradation of atrazine, since the atrazine-degrading strain *Acinetobacter lwoffii* DNS32 is able to form biofilms on iron biochar composites (Tao et al., 2019).

It is noteworthy that metal-biochar composites have also been adopted as novel catalysts, initializing the generation of reactive oxygen species (ROS) in persulfate (PS) and peroxymonosulphate (PMS) systems (Figure 5). Doping biochar with CuFe₂O₄ enhanced electron transfer, facilitating O₂ reduction to O₂ (Figure 5a). The resulting O₂ was responsible for catalysing the redox pair cycles of Fe(II)/Fe(III) and Cu(I)/Cu(II). The Cu(I) and Fe(II) species generated during this process then catalysed the formation of

SO₄[•], enhancing the *o*-nitrochlorobenzene degradation in soil (Zhao et al., 2020). Nano zero valent iron (nZVI)-biochar composites were used as a catalyst to activate peroxy-monosulphate for atrazine degradation (Figure 5b). The atrazine molecule was firstly adsorbed by the nZVI-biochar composite. After, dissolved Fe²⁺ released from the composite activated peroxymonosulphate to generate ROS, including SO₄[•], $\cdot$ OH and ¹O₂. Compared with the virgin biochar and nZVI, the novel biochar composite revealed a synergistic effect on peroxymonosulphate activation and atrazine degradation (degradation rates of 40%, 55% and 96% for biochar-PMS, nZVI-PMS and biochar composite-PMS systems, respectively) (Diao et al., 2020). Considering that sulphate radical-based advanced oxidation is a low-impact remediation strategy with excellent performance (Hou, 2020), application of these biochar composites for the catalytic generation of ROS in this system aligns well with the concept of green and sustainable remediation (GSR).

4.3 | Nutrient retention

Soaking biochar or biomass feedstock directly with salts of nutrients, and applying the resulting material to soil would undoubtedly increase soil fertility. However, nutrients may be easily leached out in the long run, leading to decreased soil fertility. In contrast, applying mineral-biochar composites to soil improves soil health because of enhanced nutrient retention. Application of a Mg-Fe LDH-biochar composite favoured the retention of NH₄⁺ (via hydrogen bonding) and NO₃ (because of anion exchange) while simultaneously immobilizing toxic metals (Zhang et al., 2018) (Figure 2). Biochar composite prepared via co-pyrolysis of spruce residues and the biomass combustion ash reduced the loss of K during leaching and allowed a higher plant K use efficiency (Buss, Jansson, & Mašek, 2019). Potassium-iron biochar composites reduced the leaching of PO₄³⁻ and NO₃ from soil, while increasing the plant available fractions of K, Ca, PO₄³⁻ and NO₃ in soil by 22% to 78% (Chandra et al., 2020). The reduced loss of soil nutrients along with an increase in nutrient bioavailability suggest that such biochar composite can be used as a fertilizer (Chandra et al., 2020). A montmorillonite-biochar composite revealed potential for the controlled release of NH₄⁺ and PO₄³⁻. The retention of NH₄⁺ was ascribed to the high CEC of the montmorillonite, while PO₄³⁻ retention resulted from ionic bonding with cations in biochar (e.g., Ca²⁺, Mg²⁺) (Chen et al., 2017). A MgCO₃-biochar composite application to soil not only enhanced PO₄³⁻ retention because of chemisorption, but also favoured water retention as a result of physical adsorption (Shen et al., 2020). Therefore, biochar composites having high adsorption capacities render the long-term retention of nutrients. An ideal biochar composite for soil fertility improvement should possess a

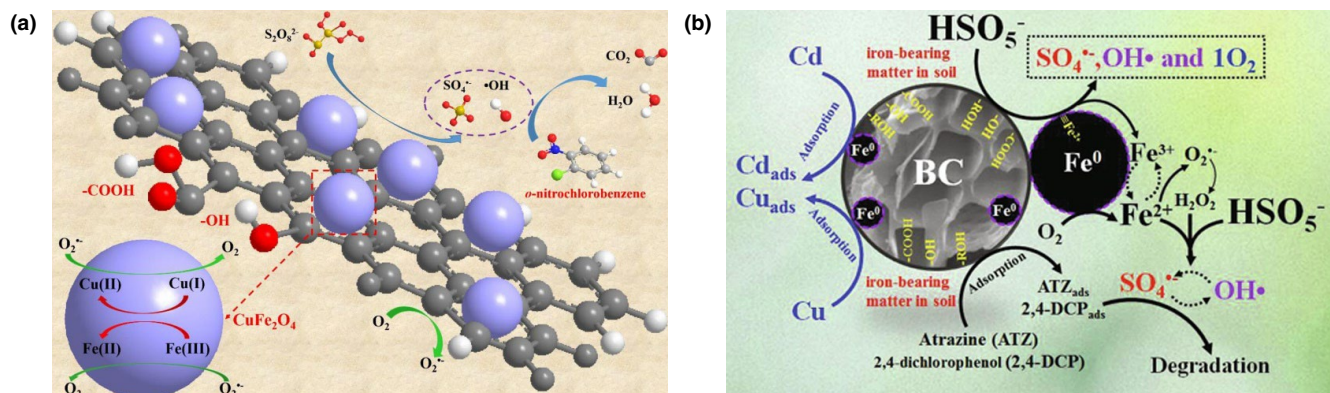


FIGURE 5 (a) Persulfate (PS) activation by a novel CuFe₂O₄-biochar composite for *o*-nitrochlorobenzene degradation. Reproduced with permission from Zhao et al. (2020). Copyright 2020 Elsevier. (b) Peroxymonosulphate (PMS) activation by nZVI-biochar composite for atrazine degradation. Reproduced with permission from Diao et al. (2020). Copyright 2020 Elsevier

well-developed pore structure and high ion exchange capacity. However, it should be noted that the adsorption of nutrients should be reversible so that nutrients can be released in turn, and be taken up by plants.

4.4 | Salinity adaptation

Salt toxicity decreases crop yield, threatening food security. As a result of osmotic and oxidative stresses, a high level of reactive oxygen species (ROS) that can damage nucleic acids and proteins can be generated (Farhangi-Abriz & Nikpour-Rashidabad, 2017; Napieraj et al., 2020). Metal oxide-biochar nano-composites have proven effective in aiding the salinity adaptation of safflower (Ghassemi-Golezani et al., 2020). Because of their high pore volumes, specific surface areas and CECs, both MgO- and MnO-biochar nano-composites adsorb sodium effectively, thus reducing sodium uptake by plants. Furthermore, magnesium and manganese are closely related to chlorophyll generation (Peng et al., 2019; Sun et al., 2001). Increased content of photosynthetic pigments after the application of these composites can also diminish the oxidative stress caused by salt toxicity (Ghassemi-Golezani et al., 2020).

4.5 | Antibiotic resistance gene suppression

The amendment of soils with biochar composites can also promote soil health via suppressing the abundance of antibiotic resistance genes (ARGs) while simultaneously increasing microbial diversity. Li et al. (2019) applied a novel struvite-humic acid biochar composite to a Zn contaminated manure soil. Although this amendment only immobilized Zn slightly by 8.6%, the abundance of

ARGs was dramatically decreased by 37.2% after 56 days. Bacterial community analysis indicated that the addition of biochar composite increased soil microbial diversity and decreased the abundance of the source phylum of ARGs. Similarly, Li, Wang, et al. (2020) found that variations in bioavailable Cu concentration in soil may contribute to the fluctuation of ARG abundance. The decreased bioavailable metal content because of biochar composite addition accounted for the suppression of ARGs, but the mechanisms remained unknown.

4.6 | Climate change mitigation

Biochar production and its storage in soils are promising methods of abating climate change. It has been suggested that the global implementation of biochar would offset 12% of current anthropogenic CO₂-C equivalent GHG emissions (Woolf et al., 2010). Although biochar alone can reduce global GHG emissions, recent evidence has shown that the application of biochar composites to the soil, rather than the virgin biochar, could further mitigate climate change in two distinct ways.

Both the retention of biomass carbon in biochar and its stability can be enhanced in certain types of biochar-based composites as compared with pristine biochar (Buss et al., 2019). Evidence has shown that co-pyrolysis of biomass feedstock and minerals increases biochar carbon stability. Li et al. (2014) noticed that carbon retention of calcium dihydrogen phosphate [Ca(H₂PO₄)₂]-biochar composite increased by 29% compared with untreated rice husk biochar, possibly because of enhanced aromaticity as confirmed by ¹³C NMR and FTIR analysis. Minerals would increase biochar aromaticity via enhancing the cross-linking between the less stable aliphatic fraction into condensed aromatic moieties (section 2.2) (Rawal et al., 2016). An increase in

aromaticity renders long-term carbon stability (Wang, O'Connor, et al., 2020). Apart from elevating aromaticity, minerals may also interact with biomass directly during pyrolysis, forming stable chemical bonds. Ahmad et al. (2019) observed that silica–biochar composites synthesized via ball milling and co-pyrolysis possessed the highest carbon sequestration potential. The stable bond of Si-C formed during fabrication accounted for the high stability of resulting biochar composite. Liu, Gao, et al. (2020) found that vermiculate addition increased biochar carbon stability through the formation of Si-O-C and Fe-O bonds.

Applying biochar composites to soil could regulate soil GHG emissions. For example, negative priming was observed for a coastal wetland soil amended with an iron–biochar composite. The addition of the iron–biochar composite caused the formation of large aggregates (i.e., 0.25–1 mm) where soil organic carbon was stabilized (Liu, Kong, et al., 2020). Applying a novel rhamnolipid–biochar composite to oil-contaminated soil was shown to enhance the biodegradation of petroleum hydrocarbons, while reducing the emissions of N₂O. However, soil GHG emissions in biochar composite amended soils are regulated both by the type of biochar composite applied and the soil properties. Our previous study showed that biochar would be more effective in GHG emissions reduction for coarse-textured soils than fine soils ($p < 0.05$) (Wang, O'Connor, et al., 2020). The formation of more water-stable aggregates in coarse soils may account for this phenomenon.

4.7 | Safety concerns associated with composite application

Biochar has dark sides (Godlewska et al., 2021). The release of toxic polycyclic aromatic hydrocarbons (PAHs) and toxic metals after soil amendment (Godlewska et al., 2021), the re-mobilization of soil contaminants because of facilitate transport by biochar colloids (Hameed et al., 2021), the faded performances as a result of long-term aging (Wang, O'Connor, et al., 2020) have raised a debate whether this 'black gold' can be applied safely.

So do biochar composites. Apart from the safety concerns raised by toxic chemicals during their fabrication (section 3), toxic effects of biochar composites to organisms in the entire ecosystem must not be overlooked. For instance, graphene and CNT nanoparticles on the biochar surface may induce toxic effects on living organisms via different mechanisms, such as cytotoxicity, oxidative stress, and deactivation of proteins (Hu & Zhou, 2013). Furthermore, microorganisms inoculated in biochar may further act as invasive species, causing ecological disaster after composite application (Clout & Williams, 2009). Prior to field application of biochar composites, these safety concerns should be carefully taken into account.

5 | FIELD IMPLEMENTATION: SUCCESSES AND LESSONS

Although a number of studies have tested the feasibility of biochar composites in various environmental applications, evidence from the field experiments are still very rare. However, conclusions drawn from the limited number of extant field implementations provide valuable information on how useful these composites are in practical applications (Table 4).

Iron–biochar composites can immobilize toxic metals and metalloids successfully at the field scale. For instance, applying iron–biochar composite at a low rate (i.e., 1.5 t ha⁻¹) to a rice paddy decreased the bioavailable forms of As and Cd by 26% and 36%, respectively, within 20 months (Pan et al., 2019). Considering that iron oxides are easy to obtain, and that the synthesis method is quite simple, iron–biochar composites may be a promising candidate for large scale applications. Furthermore, iron–biochar composites can also increase phosphorus bioavailability. Wu et al. (2020) suggested that because of the high isoelectric points of the amorphous iron oxides in biochar composites, phosphorus would be adsorbed and retained in the field.

Not all biochar composites perform well in field applications. Rafiq et al. (2017) produced attapulgite–biochar composites with different mixing ratios and applied these composites in pastures of the Tibetan Plateau to promote plant growth. Only when attapulgite and biochar were mixed at the mass ratio of 1:1 did the biomass increase slightly, by 12.8%. In comparison, mixing attapulgite and biochar at other ratios and applying these amendments alone, surprisingly and substantially decreased the biomass yield (by up to 47.8%). The reasons accounting for this failure remain unknown.

It should be noted that the performance of biochar composites in field studies are typically worse than those reported from laboratory studies. In the field, often positive results are observed only when biochar composites are applied at extremely high rates (e.g., 100 t ha⁻¹). It is likely that: (1) the field performances are affected by additional factors, including the climate and natural events such as flooding; (2) the influence of soil heterogeneity, which is more pronounced in the field; and (3) the raw material for large-scale composite fabrication may be of lower quality as compared with high grade chemicals in laboratory tests. For these reasons, it is suggested that more field studies should be conducted to test the applicability of additional types of biochar composites, rather than a sole focus on iron–biochar and clay–biochar composites. The roles of biochar composites in other applications, such as organic contaminant degradation/retention, GHG emissions mitigation and salinity adaptation, should also be assessed. Most importantly, the effects of various

TABLE 4 Field applications of biochar composites

Location	Field characteristics	Biochar	Application rate	Study duration	Aim of biochar composite application	Effectiveness	References
Guangdong, China	Rice paddy with 2.9 mg kg ⁻¹ Cd and 22.6 mg kg ⁻¹ As, soil pH 4.58, organic matter content 1.5%	Iron-biochar composite	1.5 t ha ⁻¹	20 months	To immobilize Cd and As	Decrease NH ₄ H ₂ PO ₄ -extractable As and DTPA-extractable Cd by 25.8% and 36.4%, respectively	Pan et al. (2019)
Tibetan Plateau	Grass land, soil pH 5.93, organic matter content 2.9%, CEC 11.9 cmol kg ⁻¹	Attapulgitite-biochar composite	3 t ha ⁻¹	3 months	To promote pasture growth	Increase biomass of pasture by 12.8% for only one type of composite, decrease the biomass for other types	Rafiq et al. (2017)
Zhejiang, China	Wheat-rice rotation agricultural land with 0.35 mg kg ⁻¹ Cd and 20.87 mg kg ⁻¹ As, soil pH 5.35, organic matter content 2%, sandy loam	Fe(II)-biochar composite	1.5 t ha ⁻¹	2 years	To immobilize Cd and As	Reduce Cd accumulation in wheat and rice grain by 16% and 57%, respectively; reduce As accumulation in wheat and rice grain by 48% and 44%, respectively	Tang et al. (2020)
Xinjiang, China	Grape field, soil pH 8.08, organic matter content 1.9%	biochar inoculated <i>Pseudomonas putida</i>	500 g biochar per tree	4 months	To improve grape quality	Increase fruit weight, soluble protein content and hardness by 7.6%, 28.6% and 10.8%, respectively	Wei et al. (2020)
Shandong, China	Coastal saline-alkaline soil, pH 8.10, organic matter content 0.8%, sandy loam	MgO-biochar composite	4.5 t ha ⁻¹	Not available	To increase phosphorus bioavailability and rice yield	Increase rice shoot biomass by 6%, increase shoot phosphorus content by 1%	Wu et al. (2019)
Shandong, China	Coastal saline-alkaline soil, pH 8.10, organic matter content 0.8%, sandy loam	Fe(II)-biochar composite and Fe(III)-biochar composite	4.5 t ha ⁻¹	2 years	To increase available phosphorus content	Increase available phosphorus content by 78.6% and 90.3% for Fe(II)- and Fe(III)-biochar, respectively	Wu et al. (2020)
Hunan, China	Rice paddy with 0.54 mg kg ⁻¹ Cd, soil pH 4.11, organic matter content 3.8%	Ash-biochar composite	10, 50, 100 t ha ⁻¹	6 months	To immobilize Cd	Decrease CaCl ₂ -extractable Cd by 77.9%, 95.1% and 96.1% for 10, 50, 100 t ha ⁻¹ group, respectively	Lei et al. (2020)

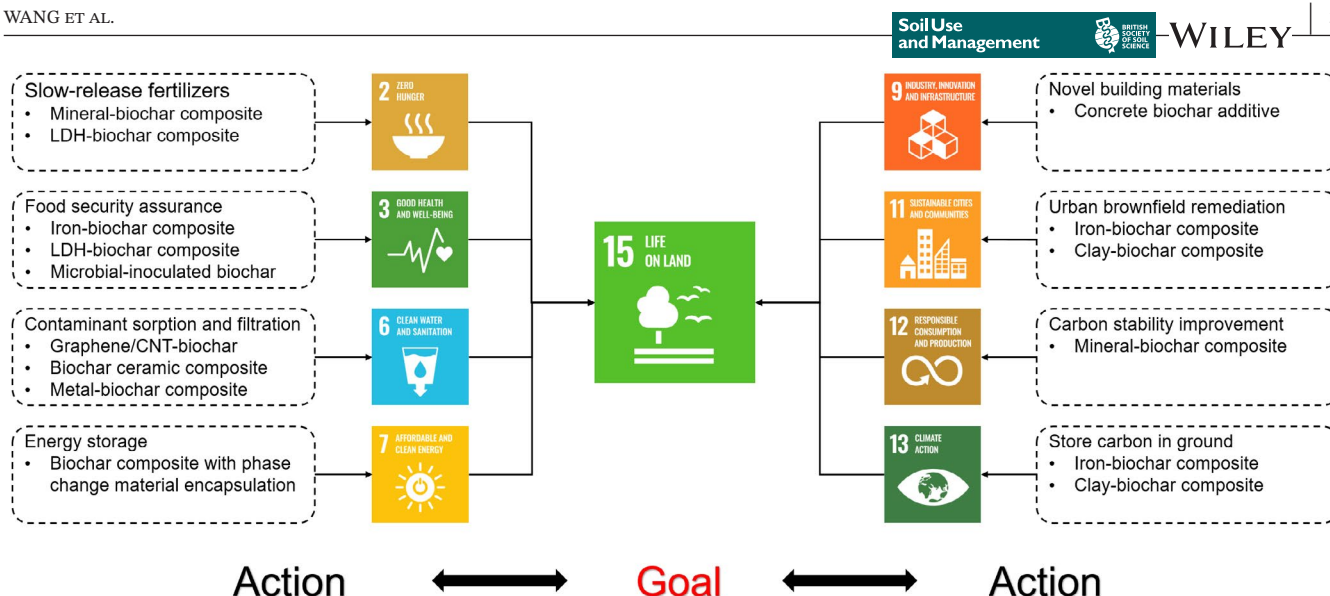


FIGURE 6 How does the application of biochar composites align with the UN's Sustainable Development Goals (SDGs)

natural forces, including temperature variations, rainfall events, wind erosion and flooding events, on the performances of biochar composites should be assessed.

6 | BIOCHAR COMPOSITE APPLICATION AND SUSTAINABLE DEVELOPMENT

The United Nations has set the ambitious Sustainable Development Goals to be achieved by 2030 (UN, 2015). To assist in the achievement of these goals, we believe that biochar composites can play vital roles (Figure 6). To protect life on land (SDG 15, the primary aim of biochar composite application), ending poverty while simultaneously preserving the environment is the key to sustainable development (Hou, O'Connor, et al., 2020). To increase the crop yield for degraded soils (SDG 2 – zero hunger), mineral-rich biochar composites as slow-release fertilizers can be fabricated in a simple way, and further used for large-scale applications (Chen et al., 2017; Hu et al., 2019). To promote human's good health and well-being (SDG 3), the application of iron-biochar, LDH-biochar and microbial-inoculated biochar composites would immobilize metals or degrade organic contaminants in soil (Diao et al., 2020; Feng et al., 2020; Gao et al., 2020). Numerous attempts have been made to improve contaminant sorption, aligning well with the principle goal of SDG 6 to obtain clean water and sanitation (Abdul et al., 2017; Heo et al., 2019; Meili et al., 2019). Novel applications of biochar composite materials, including phase change material encapsulation (Atinafu et al., 2020; Jeon et al., 2019), and concrete additives (Wang, Chen, et al., 2020) assist the achievement of SDG 7 (affordable and clean energy), and SDG 9 (industry, innovation and infrastructure). To develop sustainable

cities and communities (SDG 11), the remediation of urban brownfields with engineered iron-biochar and clay-biochar composites may be a feasible route, as field trials have already proven the effectiveness of these materials (Hamid et al., 2020; Rafiq et al., 2017). Furthermore, pyrolysing biomass into biochar has long been acknowledged as a method to displace non-renewable materials with high carbon footprints (SDG 12 – responsible consumption and production), and to store carbon in the ground (SDG 13 – climate action) (IBI, 2015; Wang, O'Connor, et al., 2020). Compared with unmodified biochar, the addition of minerals during pyrolysis (Ahmad et al., 2019; Li et al., 2014), or the application of iron-biochar composites (Liu, Kong, et al., 2020), have proven effective for the enhancement of carbon stability and negative priming, respectively.

7 | A PRACTICAL GUIDE TO SELECTION, FABRICATION AND APPLICATION OF BIOCHAR COMPOSITES

Based on aforementioned discussions, a practical guide for biochar composite selection, fabrication, and application is provided (Figure 7). Although the previous sections have assessed some of these issues, here we focus on composite selection for certain environmental applications to provide a practical reference for future biochar composite research.

For metal-biochar composites, one should bear in mind that the valence state of some metals can change (e.g., Fe), enabling oxidation-reduction reactions to occur. Therefore, if the major goal is to reduce Cr(VI) in contaminated soil or aquifer, selecting Fe(0) (Wang, Sun, et al., 2020) or Fe(II) (Liu et al., 2021) for biochar modification may be a feasible way. In comparison, Mg-doped biochar

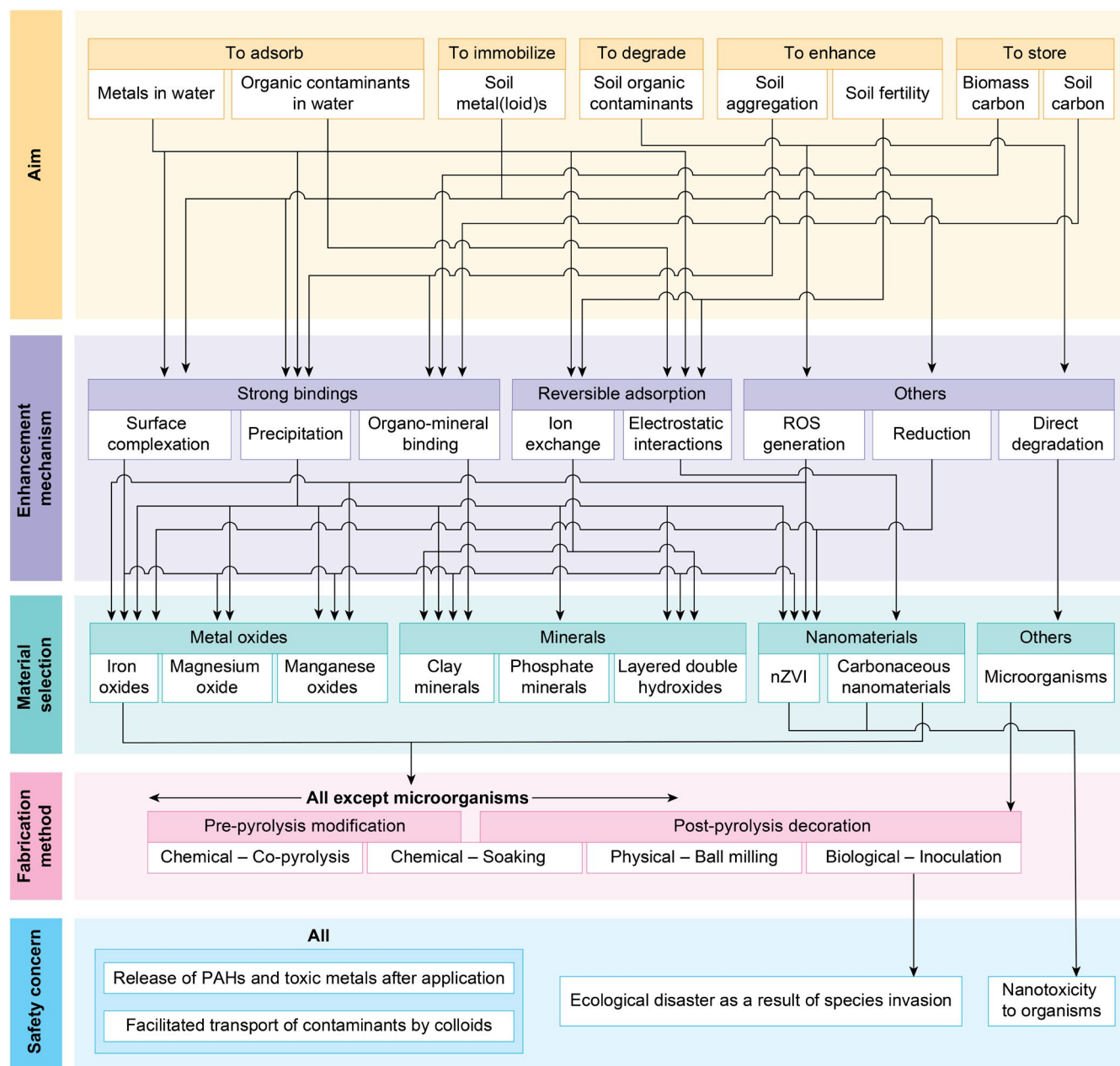


FIGURE 7 A practical guide to biochar composite application from aims, enhancement mechanisms, selection of materials, fabrication, to safety concerns

can only act as a sorbent or immobilization agent for the remediation of toxic metals (Shen et al., 2019).

Two major types of minerals are widely used for biochar modification, including clay minerals and phosphate minerals. Although LDHs are often regarded as novel, artificially synthesized lamellar materials, they can be classified as the anionic clays (Fan et al., 2014). For both cationic and anionic clay minerals, the major mechanisms are quite similar, including surface complexation/precipitation with hydroxyl, and the ion exchange with the interlayer cations/anions (Mishra et al., 2018; Wang, Rinklebe, et al., 2021). Therefore, clay minerals can be used for metal adsorption/immobilization and fertility improvement (because of reversible adsorption of nutrients). Most importantly, organo-mineral

interactions in soil is considered to be a key mechanism for long-term carbon stabilization (Hemingway et al., 2019; Yang et al., 2021). Therefore, clay-biochar composite application will promote carbon storage in ground in most cases.

Selection of a suitable clay-biochar composite for certain application is a challenge. Commonly, 2:1 clay minerals possess higher specific surface areas and cation exchange capacity, which may perform better than 1:1 clay minerals (Bergaya & Lagaly, 2013). For the fabrication of anionic clay, novel combinations of divalent and trivalent metal cations have emerged, although Mg-Al LDH is still the most common type (Zubair et al., 2021). In comparison, the aims of phosphate mineral attachment are much simpler, including metal precipitation and direct release of nutrients.

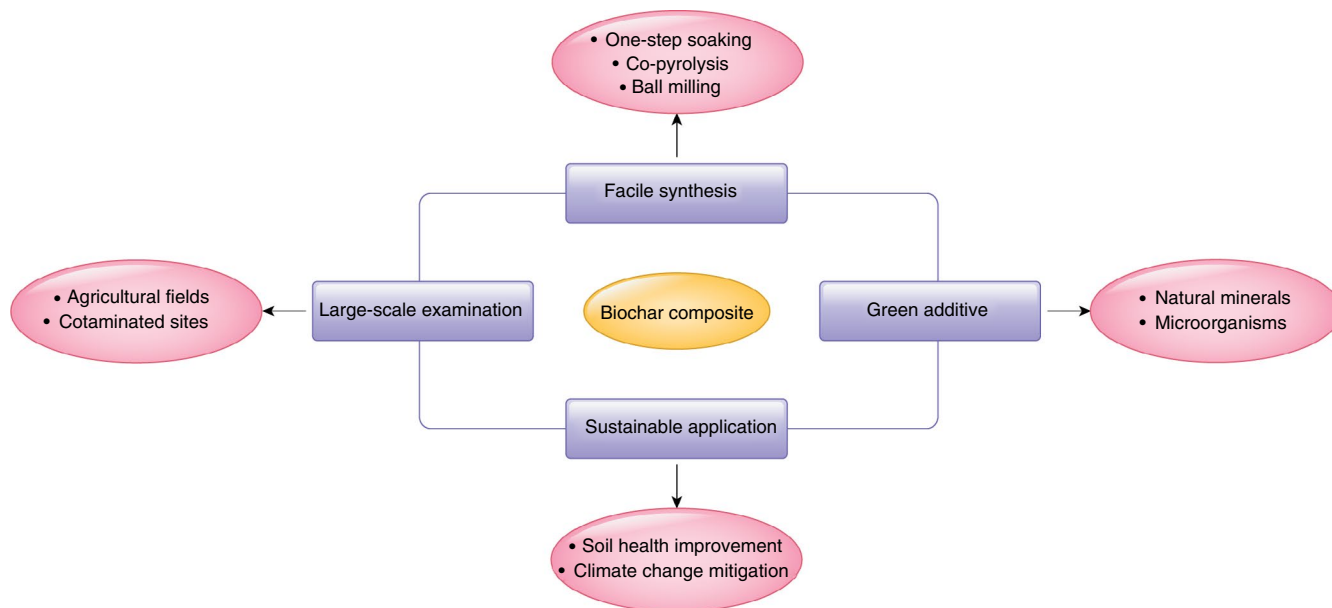


FIGURE 8 Emerging trends of biochar composite research and future directions

Nanomaterials, including nZVI and carbonaceous nanomaterials, enhance biochar performances via different mechanisms. For nZVI, it is widely used for the in-situ remediation of contaminated soil and groundwater for contaminant immobilization/reduction (Zhao, Liu, et al., 2016). In contrast, graphene and CNTs are mainly used as sorbents for contaminant removal in the aqueous solution, with C- π and π - π interactions usually being the major mechanism (Tran et al., 2017). Both types of nanomaterials raise a same concern, that is, the nanotoxicity to organisms (Keller et al., 2012; Seabra et al., 2014). Prior to field implementation and practical application of nanomaterial-biochar composites, the safety concerns raised by these materials must be carefully assessed.

Microorganism-biochar composites play unique roles in contaminant remediation, with direct degradation being the most distinct mechanism. Their fabrication methods are also unique. Unlike other types of biochar composites that can be synthesized via a wide variety of methods including ball milling, co-pyrolysis and soaking in solution, microorganisms can only be loaded onto biochar after pyrolysis production. The safety concern of these composites are also different from others. Prior to the practical application, the species to be loaded must be evaluated so that they won't lead to invasion.

8 | CONCLUSIONS

Engineered biochar composites have attracted a lot of attention during the recent years. We conclude that four novel trends have emerged, where future studies should be focused (Figure 8):

- Trend 1 – Facile synthesis of biochar composites. To realize the practical application of these novel materials, a facile fabrication method is a prerequisite. Instead of complicated multi-step methods that are costly and impractical for large-scale fabrication, future studies should develop simple synthesis methods that can achieve excellent doping performances, such as one-step modification in aqueous solution, co-pyrolysis and ball milling.
- Trend 2 – Green materials as primary doping agents. Natural minerals (clay minerals in particular) and layered double hydroxides have proven useful to enhance the performance of biochar for various purposes, including soil fertility improvement, contaminant immobilization and climate change mitigation. Microorganism-doping can also aid biochar in promoting organic contaminant biodegradation. These nature-inspired modification methods, using the power of natural materials and organisms to solve environmental problems, align well with the ongoing GSR movement. Tackling environmental problems with inspiration from nature offers green strategies with low impacts.
- Trend 3 – Sustainable applications for soil health improvement and climate change mitigation. The novel concept of soil health regards soil as a living system that should be protected and restored with care. Climate change is among the most pressing topics in environmental studies in the last decade. More applications of biochar composites have emerged to protect soils while simultaneously storing carbon in the ground.
- Trend 4 – Large-scale field demonstrations to test the applicability of biochar composites. Numerous studies have reported excellent performances of biochar composites in the laboratory. However, field studies are extremely rare.

Future applications of these novel composites in agricultural fields and contaminated sites rely on the further development of large-scale and long-term field studies.

Undoubtedly, enhancing biochars with various doping agents is a frontier of biochar research. The development of more fabrication and enhancement methods, novel applications, and ongoing results from the field application of these emerging materials promise to provide a roadmap towards a sustainable future.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 42077118), and the National Key Research and Development Program of China (Grant No. 2020YFC1808000). This work was partly carried out with the support of 'Cooperative Research Program for Agriculture Science and Technology Development (Project No. PJ01475801)', Rural Development Administration, Republic of Korea (Prof. Yong Sik Ok).

DATA AVAILABILITY STATEMENT

Data sharing not applicable – no new data generated.

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How to cite this article: Wang, L., Ok Y. S., Tsang D. C. W., Alessi D. S., Rinklebe J., Mašek O., Bolan N. S., & Hou D. (2022). Biochar composites: Emerging trends, field successes and sustainability implications. *Soil Use and Management*, 38, 14–38. <https://doi.org/10.1111/sum.12731>